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PATENT ABSTRACTS OF JAPAN

(11)Publication number : **2008-088237**

(43)Date of publication of
application : **17.04.2008**

(51)Int.Cl. *C09K 11/59 (2006.01)*
H01L 33/00 (2006.01)
C09K 11/08 (2006.01)
C09K 11/73 (2006.01)
C09K 11/64 (2006.01)

(21)Application
number : **2006-268874**

(71)
Applicant : **KYOCERA CORP**

(22)Date of filing : **29.09.2006**

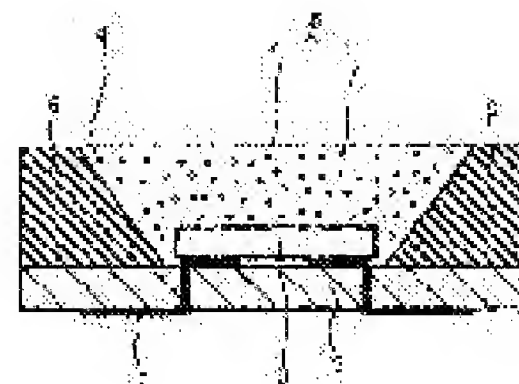
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(54) FLUORESCENT MATERIAL, WAVELENGTH CONVERTER AND LIGHT-EMITTING DEVICE

(57)Abstract:

PROBLEM TO BE SOLVED: To suppress the generation of different phase and improve the luminescent efficiency of a red light component in a light-emitting device to convert the wavelength of light emitted from a light-emitting element by a fluorescent material.

SOLUTION: The fluorescent material is expressed by formula $\text{Ba}_{3-x-y}\text{Eu}_x\text{Mn}_y\text{MgSi}_2\text{O}_8$ ($0.15 < x \leq 0.225$; $0.05 \leq y \leq 0.125$; and $1.74 \leq z \leq 2.05$), has a crystal lattice constant (a) of $5.5960 \text{ \AA} < a < 5.6064 \text{ \AA}$; and satisfies the formulas $B/(A+B) \leq 0.4$ and $C/(A+C) \leq 0.1$ wherein A is the (Cu-K α) X ray diffraction intensity of a $\text{Ba}_3\text{MgSi}_2\text{O}_8$ crystal containing Eu and Mn as activators at the peak detected near $2\theta = 31.5^\circ$ to 32° , B is the X ray diffraction intensity of a $\text{Ba}_2\text{MgSi}_2\text{O}_7$ crystal at the peak at $2\theta = 27.7^\circ$ to 28.2° , and C is the X ray



diffraction intensity of a Ba₂SiO₄ crystal at the peak at $2\theta=29.2^\circ$ to 29.8° .

JAPANESE

[JP,2008-088237,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL
FIELD PRIOR ART EFFECT OF THE INVENTION
TECHNICAL PROBLEM MEANS DESCRIPTION OF
DRAWINGS DRAWINGS

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1]

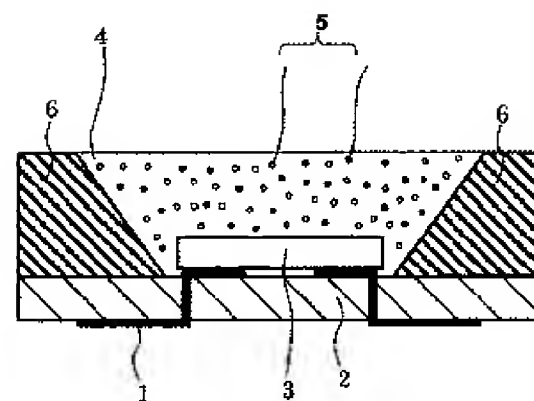
A chemical formula : It consists of a crystal expressed with $\text{Ba}_{3-x-y}\text{Eu}_x\text{Mn}_y\text{MgSi}_z\text{O}_8$ ($0.15 < x \leq 0.225$, $0.05 \leq y \leq 0.125$, $1.74 \leq z \leq 2.05$), A fluorescent substance, wherein the grating constant a of this crystal is $5.5960\text{\AA} < a < 5.6064\text{\AA}$.

[Claim 2]

A main crystal is $\text{Ba}_3\text{MgSi}_2\text{O}_8$, This crystal contains Eu and Mn as an activator, and X ray (Cu-Kalpha) diffraction intensity of a peak detected $\theta = 31.5$ degrees - near 2θ degree said $\text{Ba}_3\text{MgSi}_2\text{O}_8$ crystal is set to A, 2θ of a $\text{Ba}_2\text{MgSi}_2\text{O}_7$ crystal = X diffraction intensity of a peak in 27.7 degrees - 28.2 degrees is set to B, 2θ of a Ba_2SiO_4 crystal = a fluorescent substance when X diffraction

Drawing selection

Representative draw



[Translation done.]

intensity of a peak in 29.2 degrees - 29.8 degrees is set to C, wherein $B/(A+B)$ is less than 0.4 and $C/(A+C)$ is less than 0.1.

[Claim 3]

A wavelength converter, wherein it is a wavelength converter which outputs an outputted ray containing light which a fluorescent substance was distributing in a transparent matrix and changed wavelength of light emitted from a light source, and from which wavelength was changed and at least one ingredient is the fluorescent substance according to claim 1 or 2 among said fluorescent substances.

[Claim 4]

an ingredient of others of a fluorescent substance -- $_{10}(M, Mg)(PO_4)_6Cl_2:Eu$ (M -- Ca.) The wavelength converter according to claim 3 being at least one sort chosen from Sr and Ba, $BaMgAl_{10}O_{17}:Eu$, or $M_2SiO_4:Eu$ (at least one sort as which M is chosen from Ca, Sr, and Ba).

[Claim 5]

A luminescent device which is provided with a conductor for electrically connecting with a light emitting device which consists of a compound semiconductor which emits excitation light, and said light emitting device, and making it connect with the exterior, and a wavelength converter which changes wavelength of said excitation light on a substrate, and is characterized by said wavelength converter being the wavelength converter according to claim 3 or 4.

[Translation done.]

JAPANESE

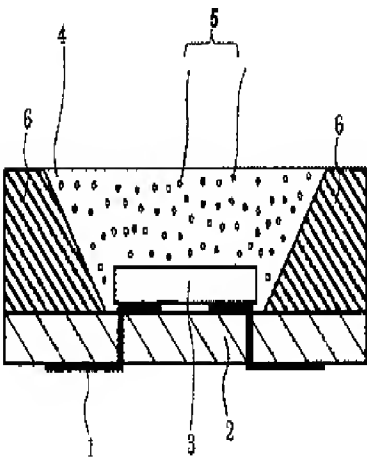
[JP,2008-088237,A]

Drawing selection

Representative draw

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION
TECHNICAL PROBLEM MEANS DESCRIPTION OF DRAWINGS DRAWINGS

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Field of the Invention]

[0001]

The fluorescent substance which this invention absorbs ultraviolet radiation or visible light, and emits the visible light of long wavelength, It is related with the wavelength converter containing the fluorescent substance which carries out wavelength changing of the light emitted from light emitting devices, such as LED (LightEmitting Diode: light emitting diode), and is taken out outside, and the luminescent device which carries a wavelength converter further.

[Background of the Invention]

[0002]

The light emitting device (it is also called the following "LED tip") which consists of semiconductor materials is small, and power efficiency colors in it skillfully well. Since it has the outstanding feature that power consumption of a LED tip is strong to the repetition of on-off lighting with a long life cycle, and low, the application to light sources for lighting of a liquid crystal etc., such as a back light source and a fluorescent lamp, is expected.

[Translation done.]

The application to the luminescent device of a LED tip is already manufactured as a luminescent device which emits light in a different color from the light of LED by carrying out wavelength changing of a part of light of a LED tip with a fluorescent substance, and mixing and emitting the light of LED by which wavelength changing is not carried out to the light concerned by which wavelength changing was carried out.

This luminescent device forms the fluorescent substance of yellow components, such as a YAG system fluorescent substance expressed with the empirical formula of $_3(\text{Y}, \text{Gd})(\text{aluminum}, \text{Ga})_5\text{O}_{12}$, on a blue LED chip.

[0003]

In this luminescent device, if the light emitted from a light emitting device is irradiated by the fluorescent substance of a yellow component, the fluorescent substance of a yellow component will be excited, and will emit visible light, and this visible light will be used as an output. However, since the light volume ratio of blue and yellow would change if the luminosity of a light emitting device is changed, the white color tone changed and there was a problem of being inferior to color rendering properties.

Then, in order to solve such a technical problem, while using the purple LED tip which has a peak of 400 nm or less as a light emitting device, Adopting as a wavelength conversion layer the structure which mixed three kinds of fluorescent substances into polymer resin, changing purple light into red and each green and blue wavelength, and emitting light in white is proposed (refer to patent documents 1). Thereby, color rendering properties can be improved.

However, in a luminescent device given in the patent documents 1, since the luminous efficiency of the fluorescent substance of a red ingredient to the ultraviolet area field near 400 nm of excitation light was low, there was a problem that efficiency of white light could not be improved.

[0004]

Although development of the fluorescent substance of a red ingredient had been performed in view of such a situation, there was no fluorescent substance which has high luminous efficiency.

for example, although the silicate system fluorescent substance was reported to the nonpatent literature 1, as a result of this inventions' conducting a trace experiment, it was markedly alike and luminous efficiency was not high. The grating constant of conventional technology (trace of the nonpatent literature 1: equivalent to the comparative example 2) is 5.6064Å. Since deposit control of an unusual appearance cannot be performed in conventional technology and it does not go into the range with optimal grating constant, the luminous efficiency of a red ingredient is low.

[Patent documents 1] JP,2002-314142,A

[Nonpatent literature 1] Appl.Phys.Lett., Vol.84, No.15-2931-2933 (2004)

[Description of the Invention]

[Problem(s) to be Solved by the Invention]

[0005]

In the luminescent device which carries out wavelength changing of the light emitted from a light emitting device with a fluorescent substance, the technical problem of this invention controls generating of an unusual appearance, and there is in improving the luminous efficiency of a red ingredient.

[Means for Solving the Problem]

[0006]

this invention person found out that luminous efficiency of a red ingredient could improve by making a preparation presentation into non-stoichiometric composition, as a result of repeating research wholeheartedly that an aforementioned problem should be solved.

That is, a fluorescent substance, a wavelength converter, and a luminescent device of this invention have the following composition.

Chemical formula : (1) It consists of a crystal expressed with $\text{Ba}_{3-x-y}\text{Eu}_x\text{Mn}_y\text{MgSi}_z\text{O}_8$ ($0.15 < x \leq 0.225$,

$0.05 \leq y \leq 0.125$, $1.74 \leq z \leq 2.05$), A fluorescent substance, wherein the grating constant a of this crystal is $5.5960\text{\AA} < a < 5.6064\text{\AA}$.

(2) A main crystal is $\text{Ba}_3\text{MgSi}_2\text{O}_8$, This crystal contains Eu and Mn as an activator, and X ray (Cu-Kalpha) diffraction intensity of a peak detected $\theta = 31.5$ degrees - near $2\theta = 32$ degree said $\text{Ba}_3\text{MgSi}_2\text{O}_8$ crystal is set to A, 2θ of a $\text{Ba}_2\text{MgSi}_2\text{O}_7$ crystal = X diffraction intensity of a peak in 27.7 degrees - 28.2 degrees is set to B, 2θ of a Ba_2SiO_4 crystal = a fluorescent substance when X diffraction intensity of a peak in 29.2 degrees - 29.8 degrees is set to C, wherein $B/(A+B)$ is less than 0.4 and $C/(A+C)$ is less than 0.1 .

(3) A fluorescent substance is distributing in a transparent matrix and wavelength of light emitted from a light source is changed, A wavelength converter with which it is a wavelength converter which outputs an outputted ray containing light from which wavelength was changed, and at least one ingredient is characterized by being a fluorescent substance given in the above (1) or (2) among said fluorescent substances.

(4) an ingredient of others of a fluorescent substance -- $_{10}(\text{M}, \text{Mg})(\text{PO}_4)_6\text{Cl}_2:\text{Eu}$ (M -- Ca.) A wavelength converter of the aforementioned (3) statement being at least one sort chosen from Sr and Ba, $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$, or $\text{M}_2\text{SiO}_4:\text{Eu}$ (at least one sort as which M is chosen from Ca, Sr, and Ba).

(5) A conductor for electrically connecting with a light emitting device which consists of a compound semiconductor which emits excitation light, and said light emitting device, and making it connect with the exterior, A luminescent device which is provided with a wavelength converter which changes wavelength of said excitation light on a substrate and with which said wavelength converter is characterized by being a wavelength converter of a statement the above (3) or (4).

[Effect of the Invention]

[0007]

According to the above (1), it consists of a $\text{Ba}_{3-x-y}\text{Eu}_x\text{Mn}_y\text{MgSi}_z\text{O}_8$ ($0.15 < x \leq 0.225$, $0.05 \leq y \leq 0.125$,

$1.74 \leq z \leq 2.05$) crystal, Since the grating constant a is $5.5960\text{\AA} < a < 5.6064\text{\AA}$, Eu and Mn doped quantity are optimized, absorption of excitation light becomes the maximum as a result and the self-absorption of luminescence can be controlled further, the luminescence intensity of a red ingredient can be improved.

According to the above (2), X ray (Cu-Kalpha) diffraction intensity of 31.5 - 32 of the $\text{Ba}_3\text{MgSi}_2\text{O}_8$ crystal

which contains Eu and Mn as an activator is set to A, 2θ of a $\text{Ba}_2\text{MgSi}_2\text{O}_7$ crystal = When X diffraction

intensity of 27.7 degrees - 28.2 degrees is set to B and $2\theta=29.2$ degree-29.8 degree X diffraction intensity of a Ba_2SiO_4 crystal is set to C, Or less by 0.4, since $C/(A+C)$ is less than 0.1 further, $B/(A+B)$ can control generating of an unusual appearance, and can improve the luminous efficiency of a red ingredient.

In the wavelength converter which outputs the outputted ray containing the light which the fluorescent substance was distributing in the transparent matrix and changed the wavelength of the light emitted from a light source, and from which according to the above (3) wavelength was changed, Since at least one ingredient is a fluorescent substance the above (1) or given in (2) among said fluorescent substances and the luminous efficiency of a not less than 600-nm red ingredient can be improved, a high luminescent characteristic and color rendering properties are realizable.

according to the above (4) -- said fluorescent substance and $_{10}(\text{M}, \text{Mg}) (\text{PO}_4)_6\text{Cl}_2:\text{Eu}$ (M -- Ca.) At least one sort chosen from Sr and Ba, or $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$, Or since it is a mixture with $\text{M}_2\text{SiO}_4:\text{Eu}$ (at least one sort as which M is chosen from Ca, Sr, and Ba), and blue and green and red luminous efficiency are very high, the luminous efficiency of the white light emitted from a mixture can be improved.

According to the above (5), since it has the above-mentioned wavelength converter, the luminescent device excellent in safety, color rendering properties, and luminous efficiency can be provided.

[Best Mode of Carrying Out the Invention]

[0008]

The fluorescent substance of this invention consists of $\text{Ba}_{3-x-y}\text{Eu}_x\text{Mn}_y\text{MgSi}_z\text{O}_8$, and the grating constant a of a crystal is $5.5960\text{\AA} < a < 5.6064\text{\AA}$. x , y , and z are $0.15 < x \leq 0.225$, $0.05 \leq y \leq 0.125$, and $1.74 \leq z \leq 2.05$, respectively. Since Eu and Mn doped quantity are optimized, absorption of excitation light becomes the maximum as a result and the self-absorption of luminescence can be further controlled if said grating constant a is in said within the limits, the luminescence intensity of a red ingredient can be improved.

The ultimate analysis of the compound presentation concerning this invention can be measured, for example using an X-ray fluorescence device, and a grating constant can be measured, for example using X-ray diffractometer.

A basic crystal structure [fluorescent substance / of this invention] is $\text{Ba}_3\text{MgSi}_2\text{O}_8$, and, as for red luminescence, Eu and Mn are coactivated by the $\text{Ba}_3\text{MgSi}_2\text{O}_8$ crystal.

However, if Ba and Mg which constitute a base material, and Si presentation change, the unusual appearance of Ba_2SiO_4 and $\text{Ba}_2\text{MgSi}_2\text{O}_7$ will deposit and the efficiency of red luminescence will fall. If the preparation presentation of Ba, Mg, and Si which constitutes a base material is set to $1.32 < (\text{Ba}/\text{Si}) < 1.57$ and $0.48 < (\text{Mg}/\text{Si}) < 0.58$, there will be few precipitation amounts of an unusual appearance and they will not influence red luminescence so much. In order to obtain higher red's luminescence intensity, it is desirable that it is $1.36 \leq (\text{Ba}/\text{Si}) \leq 1.54$ and $0.50 \leq (\text{Mg}/\text{Si}) \leq 0.56$.

[0009]

Mole-ratio x of Eu should just fill $0 < x \leq 1$ in $\text{Ba}_{3-x-y}\text{Eu}_x\text{Mn}_y\text{MgSi}_z\text{O}_8$. However, when mole-ratio x of luminescent-center-ions Eu^{2+} is too small, there is a tendency for luminescence intensity to become small, and

even if too large, on the other hand, there is a tendency for luminescence intensity to become small too by the phenomenon called concentration quenching. As a minimum, $0.02 \leq x$ is preferred and $x \leq 0.5$ is preferred as a maximum.

[0010]

The mole ratio of Mn should just fill $0.02 \leq y \leq 0.4$. However, the energy of Eu^{2+} excited in response to the exposure of the excitation light source moves the fluorescent substance of this invention to Mn^{2+} , and since it is thought that Mn^{2+} is carrying out red luminescence, the grade of energy transfer changes with presentations of Mn. So, in order to obtain red light intensity efficiently, the Mn composition of $0.075 \leq y \leq 0.15$ is preferred.

[0011]

The mole ratio of Si should just fill $1.74 \leq z \leq 2.05$. However, if the mole ratio of Si is smaller than said lower limit, green luminescence of Ba_2SiO_4 will become strong, and if a maximum is exceeded, green luminescence of $\text{Ba}_2\text{MgSi}_2\text{O}_7$ will become strong. So, in order to obtain red light intensity efficiently, Si presentation of $1.8 \leq z \leq 2.0$ is preferred.

[0012]

If it is $1.32 < (\text{Ba}/\text{Si}) < 1.57$ and $0.48 < (\text{Mg}/\text{Si}) < 0.58$ as described above, Eu of this invention and X ray (Cu-Kalpha) diffraction intensity of 31.5-32 of the $\text{Ba}_3\text{MgSi}_2\text{O}_8$ crystal which contains Mn as an activator are set to A, 2 theta of a $\text{Ba}_2\text{MgSi}_2\text{O}_7$ crystal = When X diffraction intensity of 27.7 degrees - 28.2 degrees is set to B and $2\theta = 29.2 \text{ degree} - 29.8 \text{ degree}$ X diffraction intensity of a Ba_2SiO_4 crystal is set to C, $B/(A+B) \geq 0.4$ $C/(A+C)$ can carry out to less than 0.1 further hereafter. Thereby, the luminous efficiency of a red ingredient can be improved. Although this absorbs excitation light, since it controls generating of the $\text{Ba}_2\text{MgSi}_2\text{O}_7$ crystal which does not emit light, it can increase luminous efficiency. Excitation light is absorbed, and since generating of the Ba_2SiO_4 crystal in which the short wavelength below green emits light is controlled and the abundance of the $\text{Ba}_3\text{MgSi}_2\text{O}_8$ crystal which emits a red ingredient can be increased, the luminous efficiency of a red ingredient can be increased.

[0013]

The fluorescent substance of this invention can be manufactured by heat-treating and calcinating the mixture which adjusted Ba, Mg, Eu, Mn, and the source compound of an element of Si with the mixed method of the following (A) or (B).

(A): Mixers, such as grinding, a ribbon blender, a V type blender, a Henschel mixer, etc. using dry mills, such as a hammermill, a roll mill, a ball mill, and a jet mill, or a mortar and a pestle, or a dry-blending method doubled with a mortar and mixing using a pestle.

(B): A wet-blending method which adds water etc., is mixed with a grinder, a mortar and a pestle, an evaporating dish, a stirring rod, etc. by a slurry regime or solution states using a grinder, a mortar, a pestle, etc., and is dried by spray drying, stoving, or natural seasoning.

[0014]

A latter wet-blending method is preferred also from the field from which uniform mixing is especially obtained by the whole in other element compounds in the element compounds of an activator in these mixed methods preferably [using a liquid medium, since it is necessary to make the whole mix and distribute a little compounds uniformly].

[0015]

As the heat-treatment method, in heat-resistant containers, such as alumina, crucible made from quartz, and a tray, it is 1000 °C - 1300 °C, and is made by gases, such as oxygen, nitrogen, hydrogen, and argon, being independent, or heating under a mixed atmosphere for 1 to 24 hours.

In order to control evaporation of the constituent in a heating process, it may bury and burn and may heat-treat using microwave calcination and a reducing agent.

[0016]

An atmosphere required in order to acquire the ionic state (valence) which an activation element contributes to luminescence as said heated atmosphere is chosen. In the case of divalent Eu in this invention, Mn, etc., the bottom of the neutrality of carbon monoxide, nitrogen, hydrogen, argon, etc. or a reducing atmosphere is preferred.

[0017]

Next, the wavelength converter of this invention and the lighting system which carries this wavelength converter further are explained using a drawing. Drawing 1 is an outline sectional view showing one embodiment of the luminescent device of this invention. According to drawing 1, the luminescent device of this invention is provided with the following.

The substrate 2 with which the electrode 1 was formed.

The light emitting device 3 provided on the substrate 2.

The wavelength conversion layer 4 of one layer formed so that the light emitting device 3 might be covered on the substrate 2.

The reflecting member 6 which reflects light.

[0018]

The blue fluorescent substance 5a which shows a 430 to 490-nm fluorescence in a transparent matrix, the green fluorescence substance 5b which shows a 520 to 570-nm fluorescence, and the red fluorescent substance 5c which shows a 600 to 650-nm fluorescence contain the wavelength conversion layer 4. The outputted ray containing the light which changed the wavelength of the light emitted from the light emitting device 3 which is a light source, and from which wavelength was changed is outputted.

The green phosphor 5a consists of material with around 400-nm high excitation efficiency. On the other hand, the green fluorescence substance 5b consists of material excited with the light from 400 nm to 460 nm. The red fluorescent substance 5c consists of material in which 400 nm to not only 460 nm but the light near 550 nm is excited.

[0019]

Since the number of photons emitted outside since not only the excitation light of a light emitting device but the visible light emitted from a fluorescent substance is excited by performing the above combination increases, -izing can be carried out [efficient]. That is, in the around 400-nm light emitted from a light

emitting device. The fault which the conventional fluorescent substance that excitation efficiency is low, and the excitation efficiency in around 400 nm is low since the light of the broad range in which the fluorescence of other fluorescent substances is also included is also absorbable to a thing with low fluorescence intensity emitted has is suppliable.

[0020]

(Fluorescent substance)

If a green phosphor is excited with around 400-nm light and a 430 to 490-nm fluorescence is shown, Although not limited in particular, $_{10}(\text{Sr}, \text{Ca}, \text{Ba}, \text{Mg}) (\text{PO}_4)_6 \text{Cl}_2 \cdot \text{Eu}$, $\text{BaMgAl}_{10}\text{O}_{17} \cdot \text{Eu}$, Mn , $\text{BaMgAl}_{10}\text{O}_{17} \cdot \text{Eu}$, $(\text{Ba}, \text{Eu}) \text{MgAl}_{10}\text{O}_{17}$, $_{10}(\text{Sr}, \text{Ca}, \text{Ba}, \text{Mg}) (\text{PO}_4)_6 \text{Cl}_{17} \cdot \text{Eu}$, $\text{Sr}_{10}(\text{PO}_4)_6 \text{Cl}_{12} \cdot \text{Eu}$, $(\text{Ba}, \text{Sr}, \text{Eu}) \text{aluminum}_{10}\text{O}_{17}$, $_{10}(\text{Sr}, \text{Ca}, \text{Ba}, \text{Eu})$, 6PO_4 and Cl_2 , $\text{BaMg}_2\text{aluminum}_{16}\text{O}_{25} \cdot \text{Eu}$, etc. are used (Mg , Mn). Green phosphor 5a, $[(\text{M}, \text{Mg})_{10}(\text{PO}_4)_6 \text{Cl}_2 \cdot \text{Eu}]$, (M -- the inside of Ca , Sr , and Ba -- at least one-sort) -- or $[\text{BaMgAl}_{10}\text{O}_{17} \cdot \text{Eu}]$ is used suitably.

[0021]

If a green fluorescence substance is excited with around 400-460-nm light and a 520 to 570-nm fluorescence is shown, it will not be limited in particular, but [especially] $\text{M}_2\text{SiO}_4 \cdot \text{Eu}$ (at least one sort as which M is chosen from Ca , Sr , and Ba) is used.

[0022]

0.1-50 micrometers of mean particle diameter [0.1-20 micrometers of] of the fluorescent substances 5a, 5b, and 5c are 1-20 micrometers more preferably. When mean particle diameter is larger than 50 micrometers, and the light transmittance state of the wavelength conversion layer 4 falls remarkably, the light emitted with the fluorescent substance 5 is not emitted from the wavelength conversion layer 4, but, as a result, the luminous efficiency of a luminescent device falls remarkably.

[0023]

(Wavelength converter)

The wavelength converter (wavelength conversion layer) 4 contains the fluorescent substances 5a, 5b, and 5c in a transparent matrix. The fluorescent substance 5 is directly excited with the light emitted from the light emitting device 3, respectively, and generates visible light as converted light. The converted light changed by the fluorescent substance 5 within the wavelength converter 4 is compounded, and is taken out as an outputted ray.

The thickness of the wavelength converter 4 is good to be preferably referred to as 0.2-1 mm 0.1-5.0 mm from a viewpoint of conversion efficiency. If thickness is carried out within the limits of this, the wavelength conversion efficiency by the fluorescent substance 5 can be improved, and it can control that the changed light is absorbed with other fluorescent substances. As a result, it can be outside efficient and it can be made to penetrate the visible light which was efficient to visible light, could change into it the light emitted from the light emitting device 3, and was further changed into it in it.

As for especially the peak wavelength of the outputted ray changed within the wavelength converter 4, it is preferred that it is 450-650 nm 400-750 nm. A luminous wavelength can be covered in the broad range by this, and color rendering properties can be improved.

[0024]

(Transparent matrix)

Since the wavelength converter 4 can distribute support the fluorescent substance 5 uniformly and can control the photodegradation of the fluorescent substance 5, it is preferred to form dispersedly into the transparent matrix of polymer resin, a glass material, etc. a polymers resin layer and sol -- as glass materials, such as a gel glass thin film, transparency is high and what has the endurance easily discolored by neither heating nor light is desirable.

A polymers resin layer is not limited and especially material, for example An epoxy resin, The derivative of silicone resin, polyethylene terephthalate, polybutylene terephthalate, polyethylenenaphthalate, polystyrene, polycarbonate, polyether sulphone, cellulose acetate, polyarylate, and also these materials is used. It is preferred to have the light transmittance state especially outstanding in a not less than 350-nm wavelength band. In addition to such transparency, silicone resin is more suitably used from a heat-resistant viewpoint. The glass material can illustrate silica, a titania, zirconia, and also those composite systems. Into a glass material, it is made to distribute independently, respectively and the fluorescent substance 5 is formed. Since the endurance to light, especially ultraviolet radiation is high and the endurance to heat is still higher as compared with a polymers resin layer, reinforcement of a product is realizable. Since the glass material can raise stability, it can realize the luminescent device excellent in reliability.

[0025]

(Production of a wavelength converter)

the wavelength converter 4 -- sol -- it can form by the applying method using a glass material or polymers resin layers, such as gel glass membrane. If it is the general applying method, it will not be limited, but spreading by a dispenser is preferred. For example, it is liquefied and can manufacture by mixing the fluorescent substance 5 to resin and the glass material which gave plasticity with unhardened resin, the glass material, or the solvent. As unhardened resin, silicone resin can be used, for example. Even if these resin is things of a type which mix and stiffen 2 liquid, it may be a thing of the type hardened with 1 liquid, and in the type which mixes and stiffens 2 liquid, even if it may knead the fluorescent substance 5 in both liquid, respectively or kneads the fluorescent substance 5 in one of liquid, it is not cared about. An acrylic resin can be used as resin which gave plasticity with the solvent.

The hardened wavelength converter 4 is obtained by fabricating to film state by using the applying methods, such as a dispenser, by an uncured state, or slushing into a predetermined mold and hardening. Methods of stiffening resin and a glass material include the method of using thermal energy and light energy, and also there is a method of volatilizing a solvent.

[0026]

(Luminescent device)

The wavelength converter and luminescent device of this invention are explained below using figures.

Drawing 1 is a 1 embodiment **** outline sectional view of the luminescent device of this invention. The luminescent device of this invention is provided with the conductor (electrode) 1 for electrically connecting with the light emitting device 3 which consists of a compound semiconductor which emits excitation light, and said light emitting device, and making it connect with the exterior, and the wavelength converter 4 which

changes the wavelength of said excitation light on the substrate 2. The wavelength converter 4 outputs the outputted ray containing the light which was provided with the fluorescent substance 5 currently distributed in a transparent matrix, and changed the wavelength of the light emitted from the light emitting device 3 which is a light source, and from which wavelength was changed. The luminescent device of drawing 1 is provided with the reflecting member 6.

[0027]

(Conductor)

The conductor 1 has a function as a track for electrically connecting the light emitting device 3, and is connected with the light emitting device 3 with the conductive jointing material. As the conductor 1, the metallized layer containing metal powder, such as W, Mo, Cu, and Ag, can be used, for example. When the substrate 2 comprises ceramics, a wiring conductor the conductor 1 on the upper surface Tungsten (W), When the metal paste which comprises molybdenum (Mo)-manganese (Mn) etc. is calcinated at an elevated temperature, it is formed and the substrate 2 comprises resin, mold molding is carried out and installation immobilization of the lead terminal which comprises copper (Cu), an iron (Fe)-nickel (nickel) alloy, etc. is carried out inside the substrate 2.

[0028]

(Substrate)

Since the substrate 2 is excellent in thermal conductivity and it is called for that the total reflection factor is large, the polymer resin which distributed the metal oxide particle other than charges of a ceramic material, such as alumina and nitrogen aluminum, is used suitably, for example.

[0029]

(Light emitting device)

Since the light emitting device 3 can excite a fluorescent substance efficiently, the light emitting device provided with the semiconductor material which emits the light whose center wavelength is 370-420 nm is used for it. Thereby, the intensity of an outputted ray is raised and it becomes possible to obtain a lighting system with higher luminescence intensity.

Although what emits the above-mentioned center wavelength is preferred as for the light emitting device 3, it is preferred to have the structure (un-illustrating) which equips the light emitting element substrate surface with the luminous layer which consists of semiconductor materials at the point of having high external quantum efficiency. Although various semiconductors (GaN etc.), such as ZnSe and a nitride semiconductor, can be mentioned as such a semiconductor material, if a luminous wavelength is the above-mentioned wavelength range, the kind in particular of semiconductor material will not be limited. What is necessary is just to form the laminated structure which has a luminous layer which consists these semiconductor materials of semiconductor materials on a light emitting element substrate by crystal growth methods, such as metal-organic chemical vapor deposition (the MOCVD method) and a molecular beam EPITAXIAL grown method. In order for a light emitting element substrate to make a good crystalline nitride semiconductor form with sufficient mass production nature, when forming in the surface the luminous layer which consists of nitride semiconductors, for example, materials, such as sapphire, a spinel, SiC, Si, ZnO, ZrB₂, GaN, and quartz, are used suitably.

[0030]

(Reflecting member)

The reflecting member 6 which reflects light is formed if needed, the light which escapes on the side is reflected ahead, and the intensity of an outputted ray can be raised to the side of the light emitting device 3 and the wavelength converter 4. As a material of the reflecting member 6, for example Aluminum (aluminum), nickel (nickel), Resin, such as ceramics, such as silver (Ag), chromium (Cr), titanium (Ti), copper (Cu), gold (Au), iron (Fe) and these laminated-structure things, an alloy, alumina ceramics, or an epoxy resin, can be used.

[0031]

(Production of a luminescent device)

The luminescent device of this invention is obtained by installing the wavelength converter 4 on the light emitting device 3, as shown in drawing 1. After it is possible to install the sheet shaped wavelength converter 4 hardened as a method of installing the wavelength converter 4 on the light emitting device 3 on the light emitting device 3 and also installing the material which is not hardened [liquefied] on the light emitting device 3, it is also possible to make it harden and to install.

[0032]

Although an example and a comparative example are given and the fluorescent substance, wavelength converter, and luminescent device of this invention are explained in detail hereafter, this invention is not limited only to the following examples.

[0033]

[Example 1]

Barium carbonate, magnesium oxide, a silicon dioxide, europium oxide, and manganese oxide,

By a mole ratio, as barium carbonate:magnesium oxide:europium oxide (III):manganese oxide (III):silicon dioxide:ammonium chloride =2.725:1:0.2:0.075:1.82:0.444, It mixed in the poly pot and calcinated at 1150 ** under atmospheric air after desiccation for 3 hours. Then, it calcinated by overheating for 9 hours by 1250 ** of nitrogen gas flowing down containing 12% of hydrogen, fluorescent substance

$\text{Ba}_{2.725}\text{Eu}_{0.2}\text{Mn}_{0.075}\text{MgSi}_{1.82}\text{O}_8$ was manufactured, and it was considered as Example 1.

[Example 2]

The mole ratio of a silicon dioxide and ammonium chloride was replaced with 2.051 and 0.410, respectively, and fluorescent substance $\text{Ba}_{2.725}\text{Eu}_{0.2}\text{Mn}_{0.075}\text{MgSi}_{2.051}\text{O}_8$ was manufactured like Example 1.

[Example 3]

The mole ratio of a silicon dioxide and ammonium chloride was replaced with 1.95 and 0.4, respectively, and fluorescent substance $\text{Ba}_{2.725}\text{Eu}_{0.2}\text{Mn}_{0.075}\text{MgSi}_{1.95}\text{O}_8$ was manufactured like Example 1.

[Example 4]

The mole ratio of a silicon dioxide and ammonium chloride was replaced with 2.0 and 0.4, respectively, and fluorescent substance $\text{Ba}_{2.725}\text{Eu}_{0.2}\text{Mn}_{0.075}\text{MgSi}_{2.0}\text{O}_8$ was manufactured like Example 1.

[Example 5]

It was found, the mole ratio of a silicon dioxide and ammonium chloride was replaced with **** 1.77 and 0.4,

and fluorescent substance $\text{Ba}_{2.725}\text{Eu}_{0.2}\text{Mn}_{0.075}\text{MgSi}_{1.77}\text{O}_8$ was manufactured like Example 1.

[Example 6]

The mole ratio of a silicon dioxide and ammonium chloride was replaced with 1.739 and 0.347, respectively, and fluorescent substance $\text{Ba}_{2.725}\text{Eu}_{0.2}\text{Mn}_{0.075}\text{MgSi}_{1.739}\text{O}_8$ was manufactured like Example 1.

[0034]

[Comparative example 1]

The mole ratio of a silicon dioxide and ammonium chloride was replaced with 2.105 and 0.421, respectively, and fluorescent substance $\text{Ba}_{2.725}\text{Eu}_{0.2}\text{Mn}_{0.075}\text{MgSi}_{2.105}\text{O}_8$ was manufactured like Example 1.

[Comparative example 2]

The mole ratio of a silicon dioxide and ammonium chloride was replaced with 1.702 and 0.0.340, respectively, and fluorescent substance $\text{Ba}_{2.725}\text{Eu}_{0.2}\text{Mn}_{0.075}\text{MgSi}_{1.702}\text{O}_8$ was manufactured like Example 1.

[Comparative example 3]

The mole ratio of a silicon dioxide and ammonium chloride was replaced with 1.666 and 0.333, respectively, and fluorescent substance $\text{Ba}_{2.725}\text{Eu}_{0.2}\text{Mn}_{0.075}\text{MgSi}_{1.666}\text{O}_8$ was manufactured like Example 1.

[0035]

(Evaluation)

The luminescent device shown in drawing 1 with the above-mentioned manufacturing method was produced using the fluorescent substance obtained above, and the emission spectrum when said fluorescent substance was excited at 395 nm was measured. The relative value of the luminescence intensity in the emission peak wavelength of a red component estimated evaluation from the obtained emission spectrum. The result was shown in Table 1.

The emission spectrum was measured using the spectrophotofluorometer by Shimadzu Corp., and it asked for the grating constant by the following X diffraction measurement.

[0036]

(X diffraction measurement)

X diffraction measurement of said fluorescent substance was performed on condition of the following. Namely, the powder X-ray diffractometer (MAC M18XCE by Mac Saiensu-Sha) with which the angle-of-diffraction degree error of a scanning zone consists of a X line source of CuKaalpha by which optical adjustment was carried out to less than $\Delta 2\theta=0.05$ degree is used, And the error of the angle of diffraction accompanying sample eccentricity carried out powder X diffraction measurement using 111 peaks of standard silicon on the conditions against which the angle reproducibility not more than $\Delta 2\theta=0.05$ degree is secured.

[Table 1]

ピーク のピーク)	相対強度
	100
	73
	86
	84
	84
	74
	64
	70
	66

組成	格子定数 (Å)	Euの モル比	Mnの モル比	ピーク強度(相対値)						赤成分のピーク (600nm以上の波長)	
				Ba ₃ MgSi ₂ O ₈ (A)	Ba ₂ MgSi ₂ O ₇ (B)	Ba ₂ SiO ₄ (C)	B/(A+B)	C/(A+C)	Ba ₃ MgSi ₂ O ₈ 占有率(%)	波長	相対強度
3Si _{1.82} O ₈	5.6045	0.2	0.075	100	0	0	0	0	100	627	
3Si _{2.05} O ₈	5.5975	0.2	0.075	60	40	0	0.4	0	60	627	
3Si _{1.95} O ₈	5.6032	0.2	0.075	95.7	21.6	0	0.18	0	82	627	
1Si ₂ O ₈	5.5982	0.2	0.075	85	40	0	0.32	0	68	627	
3Si _{1.77} O ₈	5.6049	0.2	0.075	100	0	4.74	0	0.05	95	627	
3Si _{1.74} O ₈	5.6052	0.2	0.075	100	0	6.2	0	0.06	94	627	
3Si _{2.11} O ₈	5.5960	0.2	0.075	55	0	45	0	0.45	55	627	
3Si _{1.70} O ₈	5.6064	0.2	0.075	100	0	13.2	0	0.12	88	627	
3Si _{1.67} O ₈	5.6071	0.2	0.075	100	0	20	0	0.17	83	627	

	蛍光体の化学組成
実施例1	Ba _{2.725} Eu _{0.2} Mn _{0.075} MgSi ₁
実施例2	Ba _{2.725} Eu _{0.2} Mn _{0.075} MgSi ₂
実施例3	Ba _{2.725} Eu _{0.2} Mn _{0.075} MgSi ₁
実施例4	Ba _{2.725} Eu _{0.2} Mn _{0.075} MgSi ₁
実施例5	Ba _{2.725} Eu _{0.2} Mn _{0.075} MgSi ₁
実施例6	Ba _{2.725} Eu _{0.2} Mn _{0.075} MgSi ₁
比較例1	Ba _{2.725} Eu _{0.2} Mn _{0.075} MgSi ₂
比較例2	Ba _{2.725} Eu _{0.2} Mn _{0.075} MgSi ₁
比較例3	Ba _{2.725} Eu _{0.2} Mn _{0.075} MgSi ₁

[0037]

As shown in Table 1, the peak intensity in an X diffraction the fluorescent substance (examples 1-6) which is within the limits of this invention, Since generating of the Ba₂MgSi₂O₇ crystal which is an unusual appearance, and a Ba₂SiO₄ crystal was controlled, the relative intensity of the emission spectrum of a red ingredient became 73 to 100%, and it was shown that the luminous efficiency of a red ingredient is high. On the other hand, since the fluorescent substance (comparative examples 1-3) whose relative value of the peak intensity in an X diffraction is outside the range of this invention could not control generating of said unusual appearance, the relative intensity of the emission spectrum of a red ingredient became 64 to 70%, and it showed that the luminous efficiency was low.

[Brief Description of the Drawings]

[0038]

[Drawing 1]It is an outline sectional view showing the structure of the luminescent device of this invention.

[Description of Notations]

[0039]

- 2 ... Substrate
- 3 ... Light emitting device
- 4 ... Wavelength converter (wavelength conversion layer)
- 5 ... Fluorescent substance
- 6 ... Reflecting member

[Translation done.]